



Influence of modification time and high frequency ultrasound irradiation on self-assembling of alkylphosphonic acids on stainless steel: Electrochemical and spectroscopic studies



Florian Roy^a, Abdeslam Et Taouil^a, Fabrice Lallemand^a, Jean-Marie Melot^a, Xavier Roizard^b, Olivier Heintz^c, Virginie Moutarlier^a, Jean-Yves Hihn^{a,*}

^a Institut UTINAM, UMR 6213 CNRS, Université de Franche-Comté, 30 Avenue de l'Observatoire, 25009 Besançon Cedex, France

^b Institut FEMTO-ST, UMR 6174 CNRS, Université de Franche-Comté, 26, Chemin de l'Épitaphe, 25030 Besançon Cedex, France

^c ICB Laboratory, UMR 6303 CNRS, Université de Bourgogne, 9, Av. Alain Savary, 21078 Dijon Cedex, France

ARTICLE INFO

Article history:

Received 9 April 2015

Received in revised form 27 July 2015

Accepted 4 August 2015

Available online 4 August 2015

Keywords:

Self-assembly

Alkylphosphonic acid

Stainless steel

Cyclic voltammetry

High frequency ultrasound

ABSTRACT

Self-assembly of alkylphosphonic acids on stainless steel was investigated under different conditions. Four different alkylphosphonic acids exhibiting alkyl chain of various size were synthesized and studied: butylphosphonic acid (C4P), octylphosphonic acid (C8P), decylphosphonic acid (C10P), and hexadecylphosphonic acid (C16P). Electrochemistry experiments were extensively carried out in order to determine electrochemical surface blocking of adsorbed layers in function of grafting time. In term of surface blocking, an 8 h modification time was optimal for all alkylphosphonic acids. Longer immersion times lead to degradation of adsorbed layers. For the first time, grafting of C16P was studied under high frequency ultrasound irradiation. Interestingly, grafting process is highly accelerated under sonication and well-covering C16P modified substrates are obtained after 1 h of immersion under ultrasound irradiation. This would allow to elaborate high-quality alkylphosphonic acids modified samples within much shorter times. Water contact angles measurements and X-ray Photoelectrons Spectroscopy (XPS) confirmed presence of adsorbed alkylphosphonic acids on stainless steel surface. A very tight link between electrochemical blocking, surface hydrophobicity and species chemical grafting was established.

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1. Introduction

Self-assembled monolayers (SAMs) are very thin (nanometer scale) coatings which can be spontaneously chemically grafted onto metal surfaces by simple immersion of the substrate in a solution containing active molecules (sub-millimolar concentration). To permit such spontaneous and strong grafting, molecules should present reactive chemical groups towards the metal. Organization of such monolayers is ensured by the presence of alkyl chains often enabling Van der Waals interactions between adjacent molecules. SAMs can provide metal surfaces with various properties. Indeed, their compact ordered structure can make them efficient barriers against corrosion [1–3]. Their chemical functionalization can be tuned as to offer wanted chemical reactivity [4–6]. Another use for these organic coatings is to improve tribological properties for lubrication [7].

Various types of SAMs have been studied during the last 25 years. Grafting can occur on clean metallic or metal oxide surfaces. In the first case, mechanical or electrochemical removal of oxide layer has to be performed before grafting. Organothiol SAMs on gold are certainly the most common example, since sulfur group presents very strong reactivity towards this metal, giving very ordered assembled monolayers. In the second case, grafting can occur directly on oxide layer. This mainly concerns organic acids such as phosphonic [8,9], carboxylic [10,11], or sulfonic [12] acids which can be grafted on aluminum [13–15], titanium [8,9,16], copper [17] or stainless steel [10,11,18] surfaces. These systems are increasingly studied as they offer the attractive possibility to work directly on oxidized surfaces without any previous treatments.

Thanks to their low toxicity, alkylphosphonic acids are good candidates for surface modification for industrial purposes. Grafting process on oxidized surfaces has been described as acid-base reaction between acid phosphonic and hydroxyl groups present on oxidized metal surface which results in covalent bonding. This latter can be mono, bi or tridentate depending on several

* Corresponding author.

E-mail address: jean-yves.hihn@univ-fcomte.fr (J.-Y. Hihn).

parameters such as metal surface state, concentration, temperature... Interest in self-assembled alkylphosphonic acid on metal substrates has grown for the past years. Grafting on nickel [19,20], cobalt chromium alloy [21], copper [17,22], alumina [23], stainless steel [18] has already been carried out. Nevertheless, to the best of our knowledge, no study has been carried out yet on the effects of alkyl chain length and modification time on self-assembly of alkylphosphonic acids on stainless steel.

In addition, in all cases, regardless to the type of SAM or metal used, low frequency ultrasound is always used during SAM grafting process. It is used for cleaning purposes [24] either prior to substrate immersion, in order to further clean the surface or either after SAM formation to remove physisorbed species or other impurities possibly gathered during immersion process. Some studies reported the use of low frequency ultrasound during grafting of thiols on gold [25,26]. Atobe et al. reported an increase in the rate and saturated amount of self-assembled adsorption of aromatic thiolate species (4-pyridinethiolate and phenylthiolate) on polycrystalline gold under low frequency ultrasound irradiation (20 kHz) while only adsorption rate was increased for aliphatic thiolate like carboxy ethane thiolate [25]. Dai et al. showed that dodecanethiol SAMs of almost defect-free structure and very low ionic permeability can be formed on polycrystalline gold under low frequency ultrasonic irradiation (40 kHz) in a short time (15 min) [26]. In spite of these very interesting results, no additional studies have been carried out on the use of ultrasound during SAMs formation. Adsorption of organic acids layers on active surfaces has also never been investigated under sonication. Moreover, the use of high frequency ultrasound on SAM grafting process has not been studied yet even if it is well known that cavitation and mechanical activities are much less aggressive at these frequencies [27–30].

In that line of work, this paper deals with grafting of alkylphosphonic acids on stainless steel. In the first part, optimal parameters are narrowed in terms of chain length and modification time. Four different alkylphosphonic acids have been synthesized for that purpose. Then, in order to decrease modification time as much as possible, high frequency ultrasound is used during grafting. Electrochemical analyses are mainly used in order to observe electron transfers through grafted layers and to determine covering rates. Water contact angles were determined to evaluate surface hydrophobicity. Spectroscopic techniques are also used to study structural properties of grafted molecules.

2. Experimental

2.1. Chemicals

De-ionized water (Milli-Q, resistivity 18 M Ω cm) was distilled twice before use. 1-bromobutane (ACROS ORGANIC, 99%, 109-65-9), 1-bromooctane (ALFA AESAR, 98%, 111-83-1), 1-bromodecane (ALFA AESAR, 98%, 112-29-8), 1-bromohexadecane (ALFA AESAR, 98%, 112-82-3), hydrochloric acid (SIGMA ALDRICH, 37%, 7647-01-0), triethylphosphite (ALFA AESAR, 98%, 122-52-1), aqueous methanesulfonic acid (ALFA AESAR, 70% 75-75-2), absolute ethanol (ACROS, pure, 64-17-5), sodium hydroxide (ACROS, 97+%, 1310-73-2), Potassium hexacyanoferrate(II) trihydrate (SIGMA ALDRICH, 98.5+%, 14459-95-1), sodium sulfate (SIGMA ALDRICH, 99+%, 7727-73-3) were used as received.

2.2. Synthesis of alkylphosphonic acid compounds

All alkylphosphonate compounds were obtained following Arbuzov reaction. For butylphosphonic acid (C4P), triethylphosphite was added dropwise at 190–200 °C into a threefold excess

of refluxing 1-bromobutane under stirring within 45 min. Distillate temperature was not allowed to come over 45 °C. After further reaction (6–8 h), the mixture was cooled and excess 1-bromobutane removed by atmospheric distillation. Diethyl butylphosphonate was then obtained at 102–107 °C (20 mmHg). It was then boiled with 10–12 M aqueous hydrochloric acid for 24 h. The clear homogeneous solution was concentrated *in vacuo* to a solid residue, which was dried at 80 °C for 2 h. Recrystallisation in acetone/cyclohexane (1/2 v/v) afforded pure 1-butylphosphonic acid (yield: 85%).

Syntheses of octylphosphonic acid (C8P) and decylphosphonic acid (C10P) were carried out following published procedure [15] using 1-bromooctane and 1-bromodecane as starting compound, respectively.

Diethyl hexadecanephosphonate was obtained according to the same procedure from 1-bromohexadecane. Acidic hydrolysis to corresponding phosphonic acid (C16P) was different: diethyl hexadecanephosphonate was mixed with 70% aqueous methanesulfonic acid and boiled during 24 h (bath temperature: 180 °C). Water was then added and the mixture refluxed for additional 24 h. After cooling to 75–80 °C under stirring, technical acetone was added and precipitated hexadecane-1-phosphonic acid was filtered and washed with technical acetone until mother liquors were colorless (yield: 73%).

2.3. SAMs preparation

304L stainless steel substrate (0.79 cm²) was mechanically polished (grain size 5 μ m) and cleaned in ultrasonic bath (E-ONE, 35 kHz) for 5 min. The substrate was then plunged in 3% HCl solution for few seconds in order to generate surface hydroxyl groups for proper alkylphosphonic acid anchoring. Finally, the substrate was immersed in modification solution (5 mM alkylphosphonic acid in absolute ethanol).

2.4. Sonochemical cell

High frequency ultrasound irradiation was carried out using commercial equipment (Meinhardt-M11) at 575 kHz frequency. Solution volume for experiments realized under ultrasound was 50 mL and calorimetry measurements showed transmitted power of 0.8 W.

2.5. Characterization methods

Electrochemical experiments were carried out using AUTOLAB PGSTAT30 potentiostat driven by Nova.10 software. Classical three electrodes setup was used with mercury sulfate electrode as reference electrode (MSE = 640 mV/SHE), platinum wire as counter-electrode and modified stainless steel substrate as working electrode (0.79 cm²). Electrolyte was composed of 5 mM in Potassium hexacyanoferrate (II) with 0.2 M in sodium sulfate (background salt) in pure water. Cyclic voltammograms were realized at 100 mV/s.

XPS was used to measure elemental composition in order to determine oxidation state of elements. Spectra were acquired using monochromatized Al K α radiation (1486.6 eV). X-ray radiation source operated in vacuum of 3×10^{-9} mbar. Binding energies of cores levels were calibrated in function of the C1 s binding energy set at 285.2 eV, a characteristic energy of alkyl moieties. Deconvolutions were made using mixed Gaussian–Lorentzian curves (80% of Gaussian character).

Polarization Modulation Infrared Reflection Absorption Spectroscopy data were collected from a Bruker VERTEX 70 PMA 50 equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a photoelastic modular PMA: ZnSe.

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